Study of Azure A Adsorption from Aqueous Solution onto Rice Husk

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Abstract

In this study, the removal of azure A dye from aqueous solutions using low-cost materials as adsorbent by a batch system was investigated. Experiments were carried out as a function of contact time, initial concentration, pH and temperature. The equilibrium adsorption of azure A dye on rice husk adsorbent was analyzed by Langmuir, Freundlich and Temkin models. The results indicated that the Langmuir model provides the best correlation of the experimental data. Various thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) were evaluated. Thermodynamic parameters values revealed that the adsorption of azure A onto rice husk is endothermic, spontaneous, with an increased randomness in nature. The results revealed that the azure A is considerably adsorbed on rice husk andcould be an economical method for the removal of azure A from aqueous systems.

Keywords

Rice Husk;Azure A;Isotherm; Adsorption

Introduction

The industrial wastewater usually contains a variety of organic compounds and toxic substances which are harmful to fish and other aquatic. It is well known that textile industries, pulp mills and dyestuff manufacturing discharge highly colored wastewaters which have provoked serious environmental concerns all over the world [Faria et al. (2004); Qin et al. (2009); Namasivayam et al. (2001)].

Dyes can be classified into anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [Mall et al. (2006)]. The economic removal of color from textile industry effluents remains a major problem. Many dyes and pigments, although not toxic, present an aesthetic problem and reduce photosynthetic activity in the receiving waters into which they are discharged. Many dyes are designed for their chemical stability and do not undergo biochemical degradation readily [Jain et al. (2010)]. Various treatment processes such as ozonation[Muthukumar et al. (2004); Selcuk (2005)], coagulation [Lee et al. (2006); Shi et al. (2007)], ultrafiltration [Majewska-Nowak (1989)], oxidization [Salem & El-maazawi (2000); Kim et al. (2004)], electrochemical [Song et al. (2010); Gupta et al. (2007)], photocatalytic degradation [Xia et al. (2008); Dong et al. (2010)] and adsorption [Dogan et al. (2007); Suna et al. (2010); Tan et al. (2008)] have been widely investigated to remove dyes from wastewaters.

Adsorption is one of the promising alternative techniques used for the removal of dyes from water and wastewater [Gupta &Suhas(2009)], and activated carbon is the most widely used adsorbent [Wu et al. (2005)]. However, the production of activated carbon is complex and expensive, making this technology economically inefficient. Accordingly, the critical challenge of applying the adsorption method to dye removal is to find a low-cost adsorbent that is profoundly available with a high removal capacity so adsorption can successfully compete with other dye removal techniques. This is the driving force behind further studies attempting to find an efficient low-cost adsorbent. Waste materials have recently been viewed as potential low-cost adsorbents, and many reports have been published showing their ability toadsorb various contaminants including dyes [Gupta &Suhas(2009); Wu et al. (2005); Rafatullahet al. (2010); Songet al. (2010); Deniz&Saygideger(2010); Safa&Bhatti(2011); Tehrani-Baghaet al. (2011); Moussavi&Khosravi(2011); Vargaset al. (2012)]. Rice husk, an agricultural waste, proposed as a no-cost and profoundly accessible potential dye adsorbentto account for about one fifth of the annual gross rice, 545 million metric tons, of the world, contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen [Dong et al. (2010)] which make the adsorption processes possible. And it has been successfully used to remove colored component, [Dogan et al. (2007)], metal ions [Suna et al. (2010)].

Due to the biological and chemical stability of dyestuffs in a number of conventional water treatment methods, adsorption is considered as an attractive and favorable alternate for the removal of dyes and other chemicals from wastewater streams. For an efficient adsorption process, rapid removal of the pollutants as well as a high ultimate adsorption capacity of the adsorbent is needed.

In this work, the removal of azure A from aqueous solutions has been investigated using rice husk adsorbent from aqueous solutions under different experimental conditions.The study includes an evaluation of the effects of various operational parameters such as initial dye concentration,adsorbent dose, contact time, temperature and pH on the dye adsorption process. The equilibrium sorption behavior of the adsorbents has been studied using the adsorption isotherm technique. Experimental data have been fitted to various isotherm equations to determine the best isotherm to correlate the experimental data. Thermodynamics of the adsorption process has been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined

Experimental

Adsorbent

The milled rice husk obtained from rice farms in the north of Iran, Guilan, Iran was used as an adsorbent. The milled rice husk sieved through the sieves, 50-80 mesh size particles. Then rice husk in above particle size was rinsed with distilled water to remove dust and soluble impurities and then dried at 70℃ for 12 hours in an oven before use (The heat treatment of rice husk was carried out for removing any volatiles such as moisture). The dried husks were stored in a desiccator until used.

Adsorbate

Azure A acetate was product of Sigma-Aldrich and used as received without further purification (Fig. 1). A stock solution of dye was prepared by dissolving 0.025 g of it in 50 mL of double distilled water. Working solutions of different concentrations (10–50 mg/L) were prepared by further dilutions. The concentration of the dye azure A was determined using a UV-vis spectrophotometer (Janway 6100) at a wavelength corresponding to the maximum absorbance of the dye. Calibration curve was plotted based on the absorbance versus concentration of the dye solution at the maximum wavelength of the dye using Beer′s law. A Metrohm pH meter (model 827) with acombined double junction glass electrode was used toshow pH values.pH adjustments were carried out using dilute NaOH and HCl solutions.

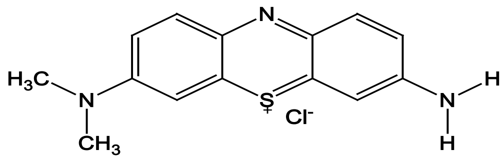

FIG.1 CHEMICAL STRUCTURE OF AZURE A

Adsorption Experiment

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature, and adsorbate concentration. The experiments were carried out in 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The pH of the solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The flasks were shaken for the required time period in a water bath shaker. For the thermodynamic study, the experiment was performed using 0.20 g rice husk added to 100 mL of azure A solution in 250 mL flasks at the different temperature. The flasks were shaken at 120 rpm for 60 min at pH 6. The initial azure A concentration used in this study was 20 mg/L. A mixture of 0.2 g of rice husks with 100 mL azure A solutions of 20 mg/L concentrations was shaken at 120 rpm for 60 min at 25℃. The initial pH of the solution was adjusted to 6. All experiments were performed in duplicate. The filtrate samples were analyzed for the determination of the final concentration of azure A by using an UV–vis spectrophotometer (Janway 6100) set at a wavelength of 598 nm, maximum absorbance. The azure Aconcentration retained in the adsorbent phase was calculated according to

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

where $C_o$and C_e are the initial and equilibrium concentrations (mg/L) of azure A solution, respectively; V is the volume (L), and W is the weight (g) of the adsorbent.

Results and Discussions

Effect of pH

The effect of pH on the removal efficiency of azure A was studied at different pH ranging from 2.0 to 12.0 and results are shown in Fig. 2. It can be seen that adsorption of azure A was minimum at solution pH 2 and increased with pH up to 6.0 and then remained

nearly constant over the initial pH ranges of 6–12. The observed low absorption rate of azure A on the rice husk at pH less than6 may be because the surface charge becomes positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. To decrease acidity of the solution, the functional groups on the adsorbent surface become deprotonated resulting in an increase in the negative charge density on the adsorbent surface and facilitate the binding of dye cation. The increase in dye removal capacity at higher pH may also be attributed to the reduction of H^+ ions which compete with dye cations at lower pH for appropriate sites on the adsorbent surface. However, with increasing pH, this competition weakens and dye cations replace H^+ ions bound to the adsorbent surface resulting in the increased dye uptake.

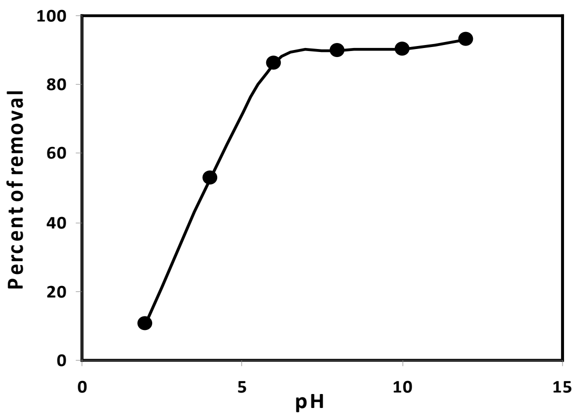

FIG.2 EFFECTS OF PH ON AZURE A DYE REMOVAL AT VARIOUS CONCENTRATIONS (ABSORBENT DOSAGE: 0.20 G; CONTACT TIME: 120 MIN; TEMPERATURE: 25℃).

Effect of Adsorbent Dose

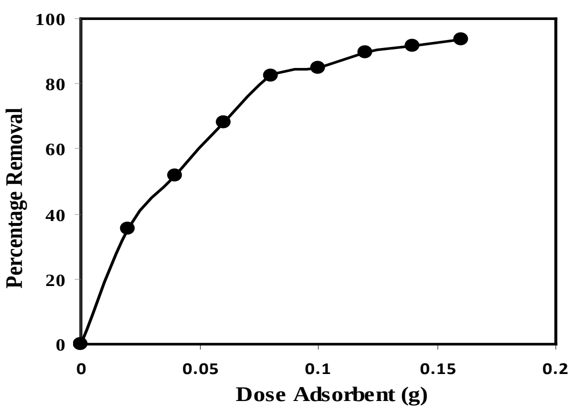

FIG.3 EFFECTS OF CONTACT TIME OF THE DYE REMOVAL AT VARIOUS CONCENTRATIONS (ADSORBENT DOSAGE: 0.2 G; PH: 7.0; TEMPERATURE: 25℃).

Fig. 3 shows the effect of adsorbent dose (rice husk) on the removal of azure A at C_o=20 mg/L and 25℃. It can be seen that the azure A removal increases with increment in rice husk up to 0.40 g, thereafter remained fairly constant despite an increase in the amount of the rice husk to 0.4 g. At the equilibrium time, the % removal increased from 34.67 to 80% for an increase in rice husk dose from 0.05 to 0.40 g. The increase in % removal was due to the increase of the available sorption surface and availability of more adsorption sites.

Effect of Contact Time on Dye Removal

Adsorption of azure A was measured at given contact times for the different initial azure A concentrations from 10 to 20 mg/L. From Fig. 4, the plot reveals that the percent azure A removal is higher at the beginning; whichis probably due to a larger surface area of the rice husk available at the beginning for the adsorption of azure A. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Most of the maximum percent azure A removal was attained after about 90 min of shaking time at different concentrations. The increasing contact time increased the azure A adsorption and it remained constant after equilibrium was reached in 40 min for different initial concentrations.

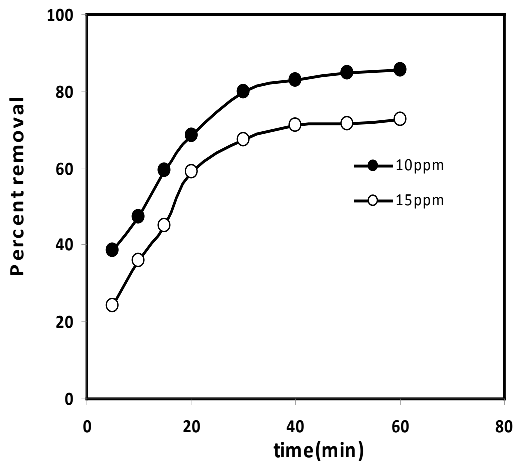

FIG. 4 EFFECTS OF DOSAGE ADSORBANT ON AZURE A DYE REMOVAL AT VARIOUS CONCENTRATIONS (CONTACT TIME: 120 MIN; PH: 7.0; TEMPERATURE: 25℃).

Effect of Initial Dye Concentration

The effect of the initial concentration in the range of 5 to 30 mg/L on adsorption was investigated and is shown in Fig. 5. It is evident from this figure that the percentage azure A removal decreased with the increase in initial concentration of azure A. The initial dye concentration provides the necessary driving force

to overcome the resistances to the mass transfer of azure A between the aqueous phase and the solid phase. The increase in initial dye concentration also enhances the interaction between azure A and rice husk. Therefore, an increase in the initial concentration of the enhances the adsorption uptake of the. This is due to the increase in the driving force of the concentration gradient produced by the increase in the initial azure A concentration. While the percentage azure A removal was found to be 89.59% for a 5 mg/L initial concentration, this value was 59.10% for 30 mg/L.

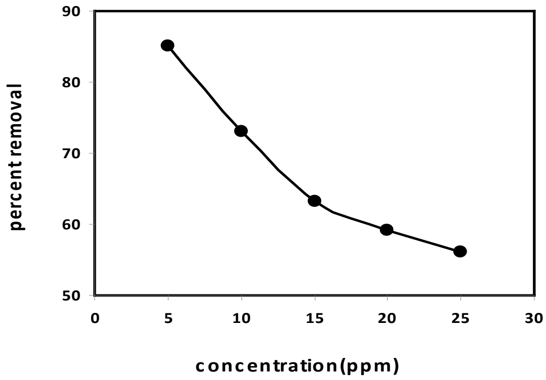

FIG.5 EFFECT OF INITIAL CONCENTRATION AZURE A ON ITS SORPTION ONTO RICE HUSK (ABSORBENT DOSAGE: 0.20 G; CONTACT TIME: 120 MIN; TEMPERATURE: 25℃).

Thermodynamic Studies

The thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations [Anirudhan&Radhakrishnan (2008)]:

$$\Delta G° = -RT \ln K \quad (2)$$

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{T} \quad (3)$$

whereK_C is the distribution coefficient for adsorption and determined as:

$$K = \frac{C_{Ae}}{C_e} \quad (4)$$

whereC_{Ae} is the equilibrium dye concentration on the adsorbent (mg L^{-1}) and C_e is the equilibrium dye concentration in solution (mg L^{-1}).

In order to explain and confirm the mechanism of azure A adsorption onto rice husk, the thermodynamics of adsorption wasevaluated using ΔG°, ΔH°, and ΔS°, given by Eqs. (2) and (3). As seen in Table 1, the value of ΔG°for all tested temperatures was calculated to be negative, which suggestedthat the adsorption of azure A onto rice husk is spontaneous and indicatedthat rice husk has a high affinity for the adsorption of azure A from solution under experimental conditions [Crini (2008)]. Values of ΔG° between −20 and 0 kJ/mol indicate a physical adsorption process [Almeida et al. (2009)]; thus the results of thermodynamic investigation reconfirmed the hypothesis of physicosorption of azure A onto rice husk. Furthermore, the values of ΔH°and ΔS°in the present experiment were 17.67kJ/mol and 67.83 J/(mol K), respectively. A positive value of ΔH°proves that the adsorption phenomenon is endothermic [Cheung et al. (2007)]. Also, the positive value of ΔS° (67.83 J mol^{-1} K^{-1}) reflects the affinity of the treated rice husk for azure A and an increased randomness at the solid-solution interface during adsorption [Liu & Liu (2008); Jain&Jayaram (2010)].

TABLE 1 THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF AZURE A ONTO RICE HUSK

Temperature (℃)	ΔG°(kJ/mol)	ΔH°(kJ/mol)	ΔS°(J/mol)
15	-1.88	17.67	67.83
25	-2.54	17.67	67.83
35	-3.48	17.67	67.83
45	-3.88	17.67	67.83

Adsorption Isotherms

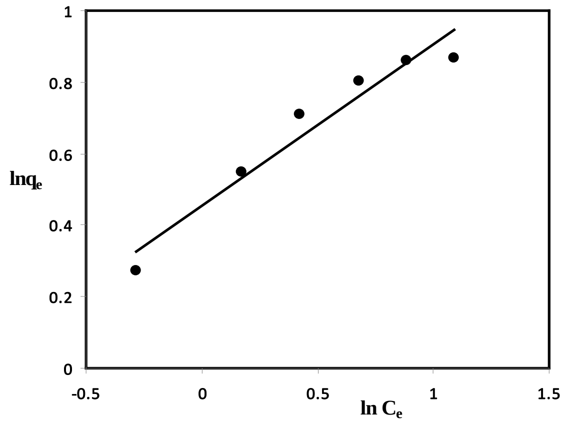

FIG.6FREUNDLICH ADSORPTION ISOTHERM AZURE A -RICE HUSK SYSTEM.

The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step toestablish a suitable model that can be used for design purpose. The adsorption capacity of this system has beeninvestigated with the Freundlich, Langmuir and Temkin adsorption isotherms. The cadmium sorption isotherm followed the linearized Freundlich model, as shown in Fig. 6. The relation between the azure A uptake capacityq_e (mg/g) of adsorbent and the residual azure A concentration C_e (mg/L) at equilibrium is given by

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where the intercept, ln K_F, is a measure of adsorbent capacity, and the slope 1/n is the sorption intensity. The isotherm data fited the Freundlich model well (R^2=0.98). The values of the constants K_F and $\frac{1}{n}$were calculated to be 2.85 and 0.45, respectively. Since the value of 1/n was less than 1, it indicated a favorable adsorption. Though The Freundlich isotherm has been more widely used, it fails to provide information on the monolayer adsorption capacity, in contrast to the Langmuir model.

The Langmuir equation relates the solid phase adsorbate concentration (q_e) or uptake to the equilibrium liquid concentration (C_e) as follows:

$$q_e = \frac{abC_e}{1+bC_e} \quad (6)$$

where a and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant can be seen from Fig. 7 that the isotherm data fits the Langmuir equation more poorly (R^2=0.99) than the Freundlich and Temkin equations. The values of a and b determined from Fig. 8 were found to be 8.67 mg/g and 0.55 L/mg, respectively.

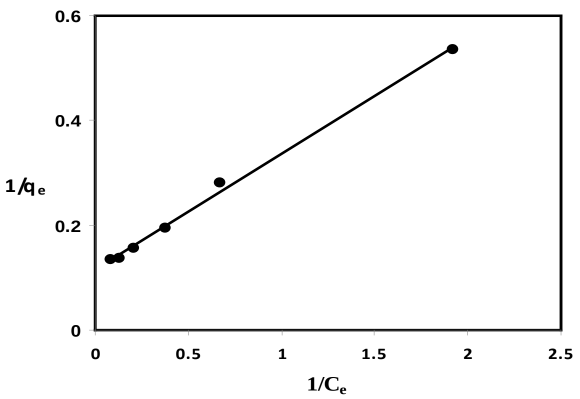

FIG.7 LANGMUIR ADSORPTION ISOTHERM AZURE A -RICE HUSK SYSTEM.

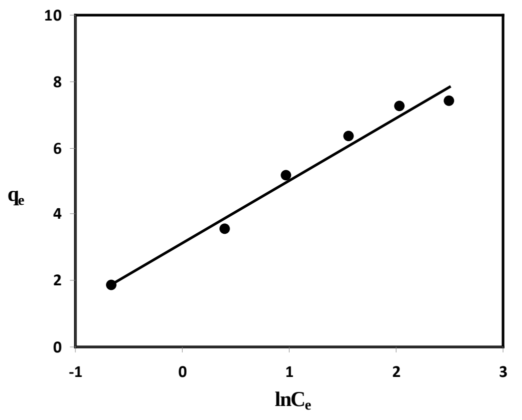

FIG. 8 TEMKIN ADSORPTION ISOTHERM AZURE A -RICE HUSK SYSTEM.

The Temkin isotherm has been used in the following form:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

Where $B = RT/b$ T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant and B correspondsto the heat of sorption.

The sorption data can be analyzed according to Eq. (7). Therefore, a plot of q_e versus lnC_e enables one to determine the constants A and B. The values of the Temkin constants A and B determined from Fig. 8 were found to be 5.22 L/g and 1.21, respectively. The correlation coefficient of 0.97 obtained showed that adsorption of azure A also followed the Temkin model.

The Langmuir isotherm is obeyed better than the Freundlich and Temkin isotherms, as evident from the values of the regression coefficients. The resulting values of the parameters K_F, n, a, b, A, B, R^2 for all the experiments in solutions with pH equal to 6.0 for maximum removal of azure A are presented in Table 2.

TABLE 2ISOTHERM MODELS CONSTANTS AND CORRELATION COEFFICIENTS FOR ADSORPTION AZURE A ONTO RICE HUSK.

parameters	a(mg/g)	b(L/mg)	R^2
LangmuirIsotherm	5.15	0.68	0.99
parameters	K_F	n	R^2
FreundlichIsotherm	2.05	2.54	0.98
parameters	A(L/g)	B	R^2
TemkinIsotherm	5.22	1.21	0.97

Conclusions

The results of this study indicated that the rice husk adsorbent can be successfully used for the adsorption of azure A dye from aqueous solutions. Adsorption is a strong choice for removal of dye from wastewater.The adsorption of azure A on rice husk reached equilibrium in 40 minutes. The equilibrium sorption data fitted the Langmuir isotherm model better than the Freundlich and Temkin models. The negative values of $\Delta G°$ and positive $\Delta H°$ obtained indicated that the azure A dye adsorption process is a spontaneous and an endothermic. Rice husk showed high adsorption capacities and it can be successfully used for treatment of azure A containing wastewater. Since this method involving less capital cost is highly efficient, it is practically feasible for developing countries. The results of this investigation will be of reference value for the removal of cationic dyes from industrial effluents.

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REFERENCES

Almeida, C.A.P., Debacher, N.A, Downs, A.J., Cottet, L.C., Mello, A.D., J. Colloid Interface Sci. 332, (2009) 46–53.

Anirudhan, T.S., Radhakrishnan, P.G., J. ChemThermodyn. 40 (2008) 702–709.

Cheung, W.H., Szeto, Y.S., McKay, G., Bioresour. Technol. 98, (2007) 2897–2904.

Crini, G., Dyes Pigments 77, (2008) 415–426.

Deniz, F., Saygideger, S. D., Bioresource Technology 101 (2010) 5137–5143.

Dogan, M., Ozdemir, Y., Alkan, M., Dyes Pigm. 75 (2007) 701–713.

Dong, Y., Han, Z., Liu, C., Du, F., Sci. Total Environ. 40 (2010) 2245–2253.

Faria, P.C.C., Orfao, J.J.M., Pereira, M.F.R., Water Res. 38 (2004) 2043–2052.

Gupta, V.K., Jain, R., Varshney, S., J. Colloid Interface Sci. 312 (2007) 292–296.

Gupta, V.K., Suhas, J., Environ. Manage 90, (2009) 2313–2342.

Jain, R., Gupta, V.K., Sikarwar, S., Hazard, J..Mater. 182 (2010) 749–756.

Jain, S., Jayaram, R.V., Desalination 250, (2010) 921–927.

Kim, T.H., Park, C., Yang, J., Kim, S., Hazard, J., Mater. 112 (2004) 95–103.

Lee, J.W., Choi, S.P., Thiruvenkatachari, R., Shim, W.G., Moon, H., Water Res. 40 (2006) 435–444.

Liu, Y., Liu, Y.J., Sep. Purif. Technol. 61 (2008) 229–242.

Majewska-Nowak, K., Desalination 71 (1989) 127–132.

Mall, I.D., Srivastava, V.C., Agarwal, N.K., Dyes Pigm. 69 (2006) 210–223.

Moussavi, G., Khosravi, R., chemical engineering research and design 89 (2011) 2182–2189.

Muthukumar, M., Sargunamani, D., Selvakumar, N., Rao, J. Venkata, Dyes Pigm. 63 (2004) 127–134.

Namasivayam, C., Radhika, R., Suba, S., Waste Manage. 21 (2001) 381–387.

Qin, Q., Ma, J., Liu, K., Hazard, J., Mater. 162 (2009) 133–139.

Rafatullah, M., Sulaiman, O., Hashim, R., Hazard, A. J., Mater. 177, (2010) 70–80.

Safa, Y., Bhatti, H. Nawaz, Chemical Engineering Journal 167 (2011) 35–41.

Salem, I.A., El-maazawi, M., Chemosphere 41 (2000) 1173–1180.

Selcuk, H., Dyes Pigm. 64 (2005) 217–222.

Shi, B., Li, G., Wang, D., Feng, C., Tang, H., Hazard, J., Mater. 143 (2007) 567–574.

Song, S., Fan, J., He, Z., Zhan, L., Liu, Z., Chen, J., Xu, X., Electrochim.Acta 55 (2010) 3606–3613.

Song, S., Fan, J., He, Z., Zhan, L., Liu, Z., Chen, J., Xu, X., Electrochim.Acta 55 (2010) 3606–3613.

Suna, D., Zhang, X., Wu, Y., Liu, X., Hazard, J., Mater. 181 (2010) 335–342.

Tan, I.A.W., Ahmad, A.L., Hameed, B.H., Desalination 225 (2008) 13–28.

Tehrani-Bagha, A.R., Nikkar, H., Mahmoodi, N.M., Markazi, M., Menger, F.M., Desalination 266 (2011) 274–280

Vargas, M.M., Cazetta, A. L., Martins, A. C., Moraes, J. C.G., Garcia, E. E., Gauze, G. F., Costa, W. F., Almeida, V. C., Chemical Engineering Journal 181– 182 (2012) 243– 250.

Wu, F.C., Tseng, R.L, Juang, R.S., J. Colloid Interface Sci. 283, (2005) 49–56.

Xia, F., Ou, E., Wang, L., Wang, J., Dyes Pigm. 76 (2008) 76–81.